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BTXs Removal with Transition Metals Coated Beds, Considering the Plausible Reaction Mechanisms

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ABSTRACT

In this study, a natural zeolite (i.e., Clinoptilolite) was used as bed of a lab scale packed tower. The bed was coated with two transition metals nano-scale particles (i.e., Fe^0 and Cu_2O). Each coated metal to bed ratio was 4.6 wt.% and the experiments were conducted in air flow of 1 L min^{-1} and temperature of 200°C. The results showed up to 83.83% of BTX (benzene, toluene and xylene) removal for Fe^0 and respectively 32.0 and 56.98% for Cu_2O and combined Fe^0-Cu_2O coated beds. However, the pollutants mineralization/elimination ratio on the combined metals coated bed, with up to 0.83, was greater than the remains which were 0.58 and 0.37 in order for Fe^0 and Cu_2O coated beds.

Key words: Air pollution, zero-valent iron, copper oxide, BTXs, clinoptilolite

INTRODUCTION

The VOCs (i.e., Volatile organic compounds) are some of the chemical compounds that are much considered today for their health threating potential and adverse environmental effects. The VOCs are emitted by anthropogenic and natural sources but, raised usage of fossil fuels and its derivatives have made the anthropogenic VOCs much bolder. Thus, the ambient and indoor concentrations of them have reported more than the recommended limits in many researches (Davil *et al*., 2011; Ohura *et al*., 2009). Hence, control of VOCs in ambient and indoor air has attracted much attentions of the health and environment authorities; also, the researchers in these fields.

From the many technologies, which have suggested or applied for VOCs source-emission control or pollution removal, the thermal destruction is a simple one that has long been used (Khan and Ghoshal, 2000). But, importance of energy saving has made the tendency for application of catalysts in the process for energy consumption declining (Papaefthimiou *et al*., 1997). Thereupon, various metals have used as catalyst agent, especially the noble metals (Scire *et al*., 2003). Although the noble metals have showed great catalytic activity; however, their cast is the restricting factor for extensive use of them.

Previous researches showed that the metals have more catalytic activity in nano scales. In this order, they have used as catalyst agents in various purposes (Piumetti *et al*., 2014; Sim *et al*., 2013). Also, the zeolites are the substances that are known as very porous and good adsorbent materials in order to use as a bed (Shen *et al*., 2014). Therefore, one can expect that coating the metallic

Table 1: Chemical constants for the BTX compounds at ambient standard conditions

Parameters	Benzene	Toluene	Xylene
Vapor pressure (pa)	12672.20	3769.30	1074.00
Octanol-water partition co-efficient (K_{ow})	150.00	480.00	1300.00
Dimensionless Henry's law constant (K_h)	0.289	0.325	0.357
Soil-air partition co-efficient (dimensionless)	47.70	150.80	332.60
Water-air partition co-efficient (dimensionless)	4.35	3.76	3.61

nanoparticles on the zeolite would enhance its catalytic properties for decomposition of VOCs on zeolite bed. Particularly in high temperatures, when desorption of VOCs from the bed takes place, thermocatalytic destruction of VOCs can result in removal of them from polluted air flow.

There are good experiences on application of transition metals as catalysts for pollution removal (Giroir-Fendler *et al*., 2014; Lu and Wey, 2007) and benzene, toluene and xylenes (i.e., BTXs) are some of the famous VOCs, which have harmful effects on human health. The BTXs are very volatile compounds with high vapor pressure and low solubility in water (Table 1) (Majumdar *et al*., 2011), which make them very potable to be present in air of polluted places.

In this regard, in the present study, the BTXs were considered as indices of harmful VOCs and removal of them was investigated. This study has focused on comparison of the BTXs elimination and mineralization on Fe^0, Cu_2O and Fe^0-Cu_2O nanoparticles coated zeolite bed. Previous studies showed adsorption of VOCs on natural zeolites such as clinoptilolite; for instance, Hernandez *et al*. (2005) showed the BTXs adsorption on clinoptilolite and they found that dealumination of the zeolite increases its adsorption capability for BTXs (Hernandez *et al*., 2005).

MATERIALS AND METHODS

Preparation of the beds: A natural zeolite (i.e., Clinoptilolite) was provided from Afraznd Inc. Iran and was used as bed. Although the miner grain size offers higher surface area, the zeolite grains with diameter of 1-2 mm were used to preventing excess head loss which can occur in finer sizes (Asilian *et al*., 2004). The zeolite was modified to enhancing the adsorption of VOCs. As described by Hernandez *et al*. (2005), it was two times washed by 1 N HCl for 6 h at 50°C with a moderate shaking and then rinsed several times by distilled water. Finally, the zeolite grains were dried at 180°C (Hernandez *et al*., 2005).

The metallic nanoparticles of Fe^0 and Cu_2O, with particle size of 30-60 nm, which were provided from Plasma Chem Inc. of Germany, were separately dispersed in distilled water with an ultrasonic device and then the dispersed particles mixed with the zeolite in a flask by slowly shaking for 2 h. Consequently, the content of the flask was dried for 10 h at 80°C. The coated nanoparticles were about 4.6 wt.% of zeolite, which was along with the similar researches. Figure 1 shows the images of the coated zeolite grains, which were taken by a light microscope system of Nikon Instruments Inc. The Coated Zeolite (i.e., CZ) was heated at 300°C for activation. Furthermore, this heating causes that the moisture and probably organic matters completely pool out.

Experiment appliances and procedure: The used reactor was a tubular steel (i.e., D = 4.5 cm and H = 30 cm) and the reactor temperature was controlled by an electrical automatic set. The reactor was filled with 200 g of the CZ and the experiment was carried out at 200°C. The air current was polluted by the BTXs compounds synthetically and the polluted air with a flow rate of 1.5 L min^{-1} was passed through the reactor during the experiments. In Fig. 2, scheme of the system is shown.

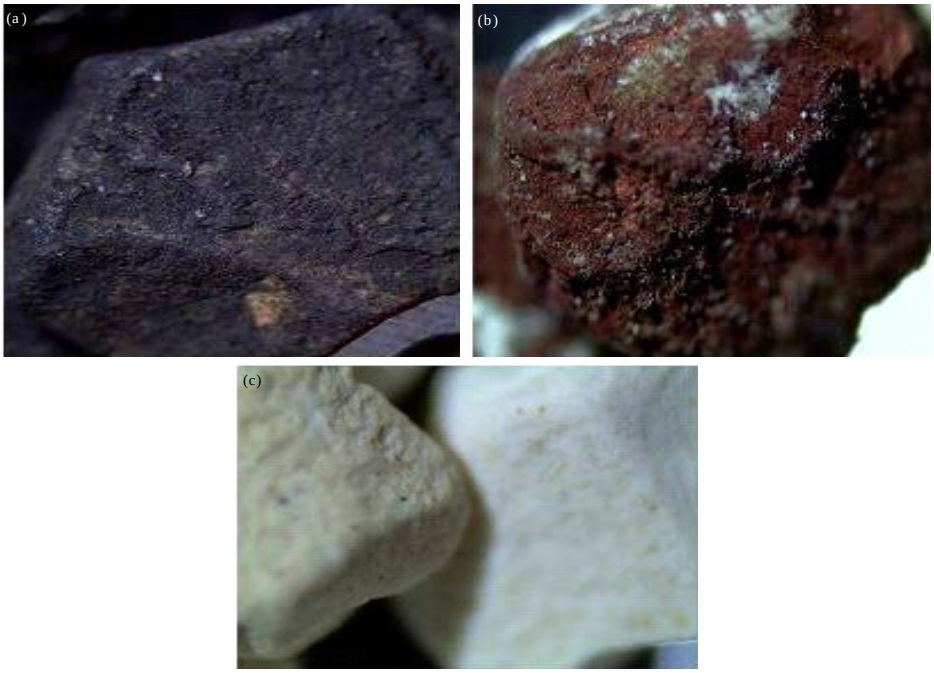

Fig. 1(a-c): Images of (a) ZVI-CZ and (b) CO-CZ and (c) C-CZ 100x magnified

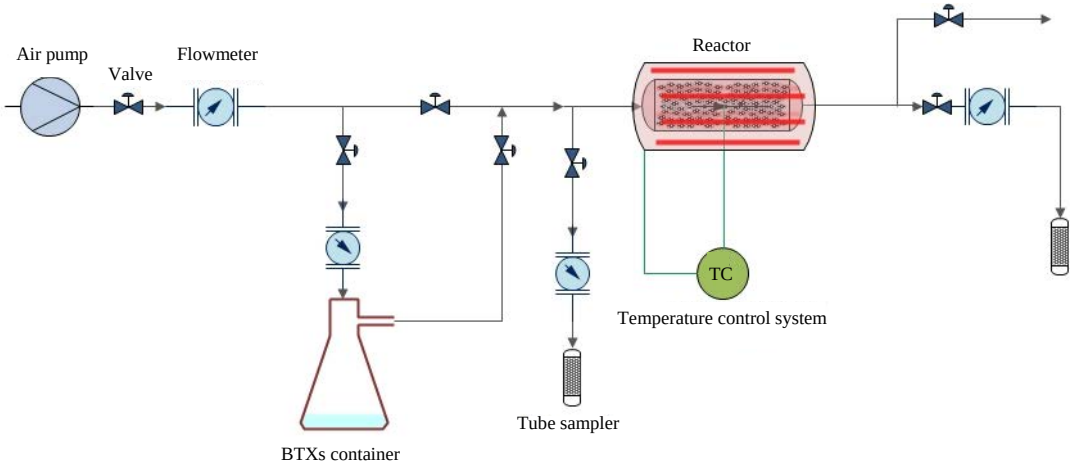

Fig. 2: Schematic view of the applied system and its accessories

Sampling and analysis: Charcoal tubes from SKC Inc. USA, were used for BTXs sampling. Sampling flow rate was 100 mL min^{-1} and the volume of each gathered sample was 2 L (Keshavarzi *et al*., 2003; NIOSH., 2003). The extraction was done by using 2 mL CS_2 in 5 mL vials. The vials were carefully shaken for 10 min during the extraction.

The extracted samples were analyzed using the GC-FID model Chrom Tech, Inc. with a 25 m silicone column with diameter of 0.32 mm and using helium as carrier gas. The 1 μL of sample was injected and the detection was performed as standard methods technique in the oven temperature of 40°C raised to 250°C during 10 min and the injection temperature of 180°C.

The concentration of CO_2 was determined by GAS-TEC Inc. Japan, CO_2detector tubes according to the factory's instructions.

The water saturation test was performed to determination of the blank volume inside the reactor and the volume of the zeolite grains in the reactor (Braja, 2001).

RESULTS AND DISCUSSION

Elimination of the BTXs: The obtained results showed the highest elimination of the BTXs compounds up to 83.8% with the zero-valent iron nanoparticle coated zeolite (i.e., ZVI-CZ). Subsequently, for copper oxide coated zeolite (i.e., CO-CZ) and 1:1 combined ZVI-CZ: CO-CZ (i.e., C-CZ), it was up to 32.01 and 56.98%. Inlet concentrations of the BTXs were some various because of simultaneously vaporization of the compounds in ambient conditions, to keep the natural condition of air pollution by the BTXs (Table 2).

Almost close removal efficiencies were seen on ZVI-CZ (SD = 1.31); however, they have not confirmed the same trend in the CO-CZ (SD = 4.57) and C-CZ (SD = 16.59).

It was found from the saturation test that, the net volume of the beds was 114.39 cc, which was indeed the occupied space of the reactor with the bed.

According to the flow rate and blank volume of the bed, a retention time of 4.7 sec was provided in the reactor. This is enough as the suggested 0.5-1 sec for thermal destruction of VOCs at 700-980°C (Khan and Ghoshal, 2000). With the retention time and the heat of 200°C, up to 83.8% of VOCs elimination was obtained. Comparing to the suggested combustion condition; although, the time is greater than 0.5-1 sec but 200°C is much lower than 700-980°C. Hence, it can be inferred that the obtained removal in the lower temperature of the experiment is evidence of the catalytic act of the bed.

As the results showed more elimination of VOCs has obtained by ZVI-CZ. Hence, it can be indicated that the Fe^0 nanoparticles were more effective in enhancement of catalytic properties of zeolite for removal of the VOCs rather than Cu_2O and a combination of Fe^0 and Cu_2O.

The Fe^0 has more electron numbers in its atomic valence layer than Cu_2O. This can be a reason for higher activity of Fe^0 in removal of the VOCs. Because in nano scales, free surface area increases and structural failures occur. Hence, the valence electrons can more participate in the reactions (Henn and Waddill, 2006; Wang *et al*., 2005). For instance, Zhang (2003) showed the catalytic features of Fe^0 and conversion of Fe^0 to Fe^{2+}, which was used for decomposition of organic compounds (Zhang, 2003). Fe^0 can turn to Fe_2O_3 with losing electron and the released electrons participate in the VOCs degradation.

Benzene: Benzene had the most inlet concentrations compared to the remains and it was removed with slightly lower performance among the other compounds in ZVI-CZ and CO-CZ (Fig. 3). One could relate the lower removal of benzene with the beds to its more molar fraction than the other compounds, as the previous researches showed the effect of higher pollution loading on these compounds elimination in an air stream (Rostami *et al*., 2014). Also, there might been other effective factors on the pollutions removal on the beds, such as chemo-physical properties. So that, adsorption of the gas molecules form air stream to surface of the bed approaches them to catalytic

Table 2: Inlet concentration of BTXs for each bed

Parameters	Benzene (ppm)	Toluene (ppm)	p-Xylene (ppm)	m-Xylene (ppm)	o-Xylene (ppm)
ZVI-CZ	66.66±7.98	9.14±4.75	3.27±1.46	2.98±0.31	1.60±0.28
CO-CZ	50.48±2.57	7.66±1.33	3.40±0.57	2.56±1.47	1.00±0.71
C-CZ	59.60±3.11	11.11±2.11	2.02±1.81	2.55±1.49	1.61±0.1

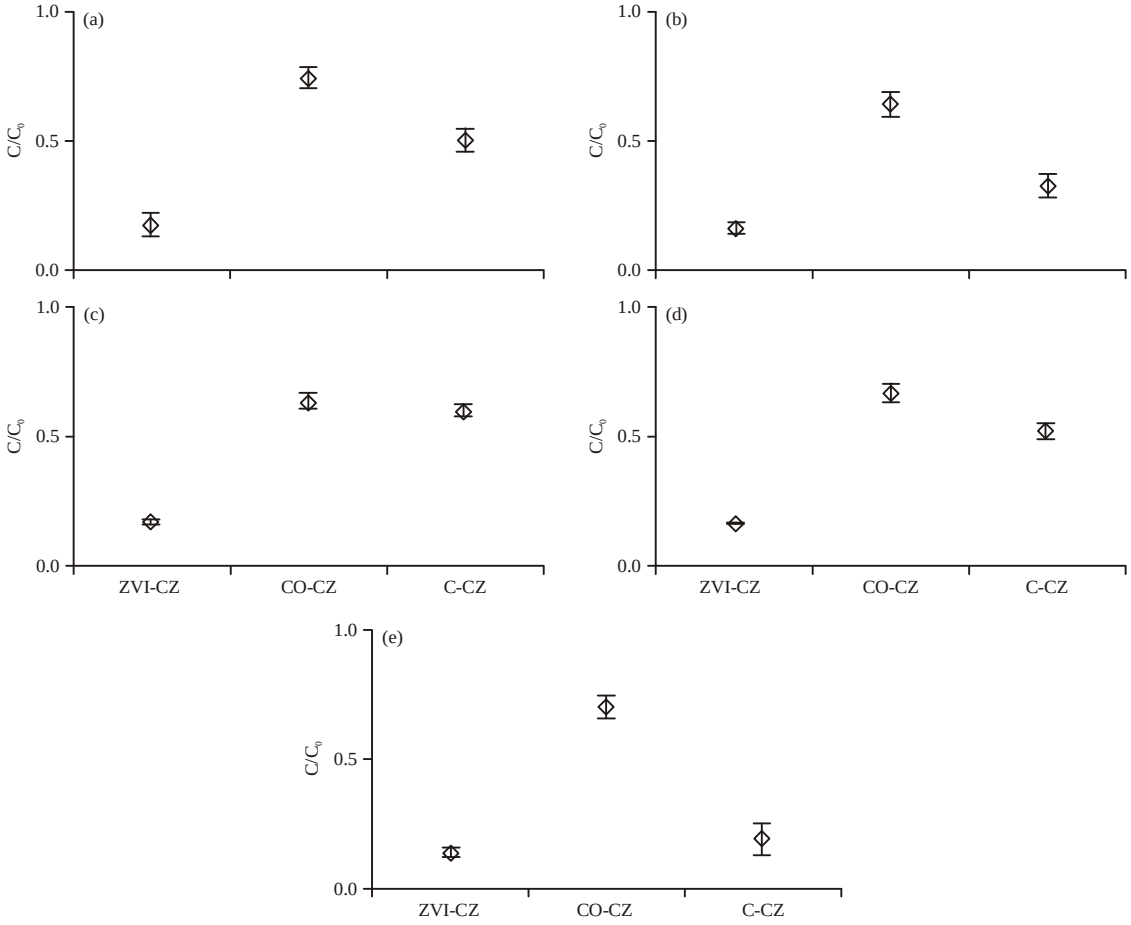

Fig. 3(a-e): Removal efficiency in the Fe^0 and Cu_2O coated beds, (a) Benzene, (b) Toulene, (c) p-Xylene, (d) m-Xylene and (e) o-Xylene

destruction with the metallic particles (Silva *et al*., 2008). Thus, we can see from the Table 1 that benzene has the most potential to desorption from the bed surface with highest vapor pressure and lowest soil-air portion co-efficient.

The VOCs reduction could be occurred by several reduction pathways on the coated beds in presence of Fe^0 and Cu_2O (Lai *et al*., 2014; Tratnyek *et al*., 1997) (Fig. 4). These reductive reactions could result in production of more hydrogenated compounds such as cyclohexane (Kim *et al*., 2004). But, the other reactions which could led to decomposition of the BTXs are oxidative reactions with production of hydroxyl free radicals ($^{\bullet}OH$) on the surface of the metallic nanoparticles (Wang *et al*., 2012). Formation of the highly reactive hydroxyl radical with the metallic nanoparticles could be happened by a mechanism analogous to the Haber-Weiss cycle (Hanna and Mason, 1992). In presence of water vapor and in high temperatures, the redox reactions can produce $^{\bullet}OH$ free radicals. These free radicals immediately and non-selectively react with VOCs molecules (Grain, 2004; Guillemot *et al*., 2007). The electrophile free radicals attack to the ligands with more electrons, so they can break the benzene ring to simpler intermediates or add OH to form phenol (Fig. 5) and then this activated molecule can react with O_2 and NO_2 to from other products (Semadeni, 1994). Decomposition of the VOCs may take place by several path ways. For example,

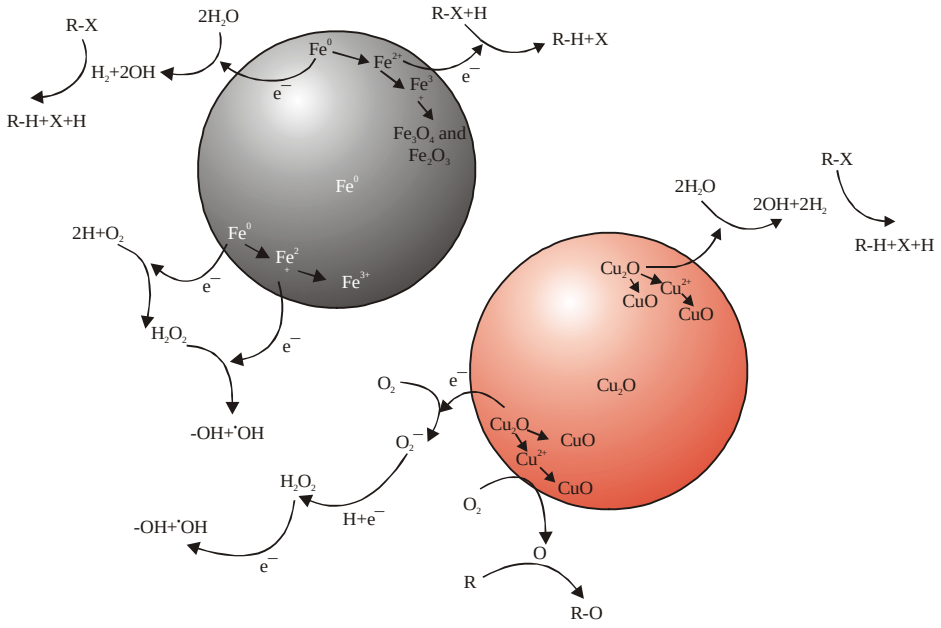

Fig. 4: Role of the Fe^0 and Cu_2O particles on oxidative and reductive reactions of the VOCs (Grcic *et al*., 2012; Li *et al*., 2006; McDowall, 2005; O'Carroll *et al*., 2013; Pham and Lee, 2014; Wang *et al*., 2014; Ziemann and Atkinson, 2012)

in presence of hydroxyl radicals, abstraction of hydrogen atoms will lead to production of some intermediates such as benzaldehyde, benzoic acid and benzyl alcohol. However, the previous researches have reported lower reaction rate constant (k) of hydrogen abstraction reactions than OH addition ones (Nichipor *et al*., 2012). The similar studies have showed that many other intermediates such as cresol, 4-methyl-2-propyl furan and formic acid may be produced, also some nitro aromatics like 4-nitrophenol may be produced by reaction of the intermediates and nitrogen (Van Durme *et al*., 2007). The intermediates for reaction of •OH with benzene are reported mainly as phenol, carbonyls and formic acid (Berndt *et al*., 1999). It is found that phenol is one of main yields of •OH initiated degradation of benzene (Volkamer *et al*., 2002). Figure 5 shows some reaction pathways of •OH initiated reactions for BTXs compounds.

Toluene: In the terms of physic-chemical properties, toluene was the next compound after benzene among the BTXs, with considerably lower vapor pressure than benzene (Table 1) which made its mole fraction in the air stream lower than benzene.

We can conclude that the lower vapor presser and higher soil-air partition coefficient could be the reason of its higher elimination in contrast to benzene (Fig. 3). Similar results about benzene and toluene are obtained by other research; also, they found that benzene has less affinity to bed among the BTXs. Furthermore, the higher reported reaction rate constant of toluene with •OH ($k = 6\times10^{12}$) than benzene ($k = 1.2\times10^{12}$) (Martinez *et al*., 2014), can be other effective reason of its higher degradation rate. However, the results showed that p-xylene and m-xylene in C-CZ had notable lower removal efficiencies than toluene; although the xylenes are less volatile than toluene (Table 1). The results showed that the compounds with lower vapor pressure had better removal;

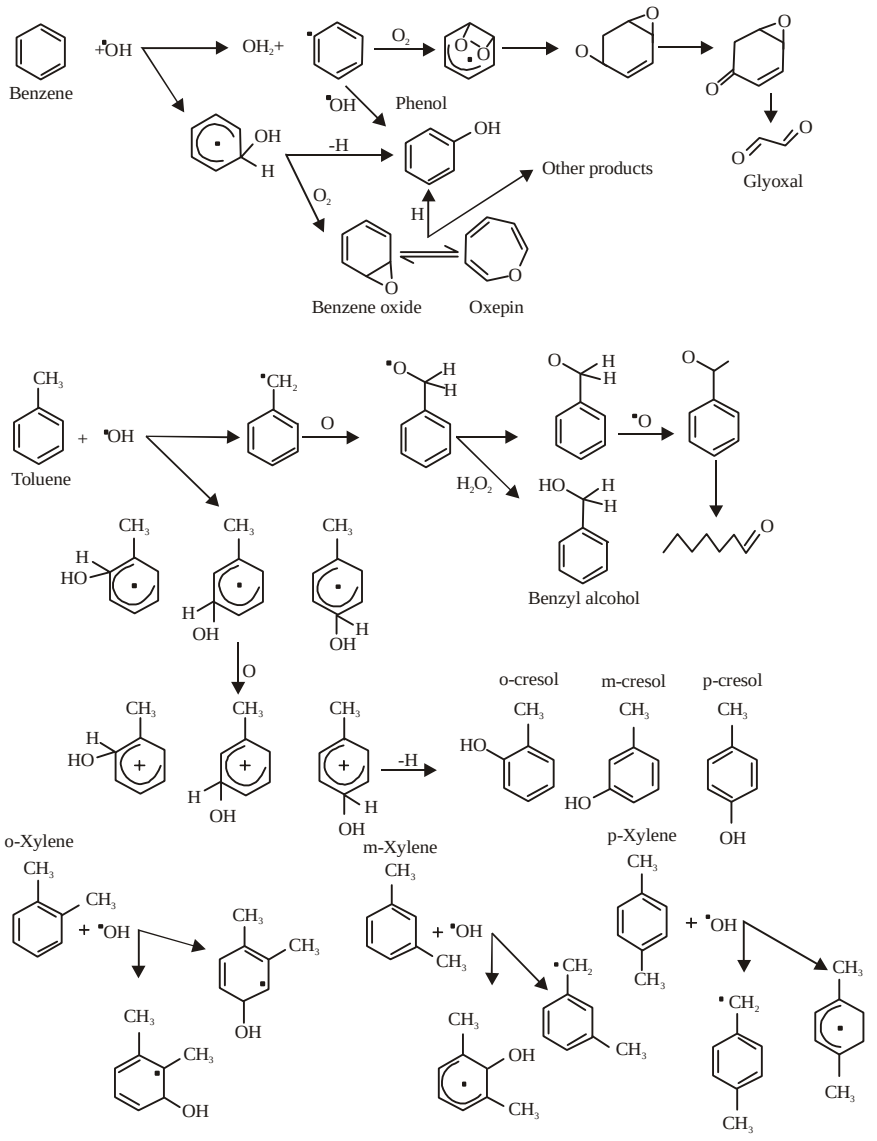

Fig. 5: Some reaction pathways of the BTXs and hydroxyl free radical (Albarran and Munguia, 2014; Benzinger, 2010; Golding *et al*., 2010; Hu *et al*., 2011; Huang *et al*., 2011; Nichipor *et al*., 2012; Qian *et al*., 2013; Volkamer *et al*., 2002; Zhao *et al*., 2005)

hence, about toluene and m and p-xylenes two scenarios can be raised. One is toluene higher degradation on the surface of metallic nanoparticles and other is its more reaction potential with non-surface free radicals than m and p-xylenes which according to the reported higher reaction rate constant of m and p-xylenes with •OH ($k = 23.4\times10^{12}$ and $k = 23.4\times10^{12}$) (Martinez *et al*., 2014), the first scenario sound to be more probable.

The reaction of toluene with •OH could led to various intermediate products; because, the OH may react with the methyl group by H abstraction or OH addition to the ring and the subsequent reactions. But, it has found that up to 65% of the reactions have been by the pathway of OH addition and around 7% for H abstraction pathway (Vivanco and Santiago, 2010).

Xylenes: In the ZVI-CZ with highest BTXs removal among the beds, o-xylene had the highest removal among the BTXs; also, among the xylenes it was the first with the highest removal and m-xylene and p-xylene were the second and third ones. Moreover, the removal trend of the xylenes was similar for the C-CZ. On the other hand, in the CO-CZ which had the lowest removal efficiency, the removal efficiency trend of the xylenes was reverse of the ZVI-CZ and C-CZ (Fig. 3).

The xylenes have the most reaction rate constant with $^{\bullet}OH$ among BTXs; thus, it is reported up to 13.7×10^{12}, 23.6×10^{12} and 14.3×10^{12}, respectively for o-xylene, m-xylene and p-xylene (Martinez *et al*., 2014); of course these rates are some different the studies, as somewhere they have suggested slightly higher rate for p-xylene than o-xylene (Benzinger, 2010). Therefore, it can be inferred that, in the ZVI-CZ which had the highest removal efficiency, the bed has the most catalytic activity and with more production of the free radicals degraded the BTXs. So, the xylenes which have higher reaction rate with the free radicals have been more degraded. On this basis, in CO-CZ with the lowest catalytic activity, elimination of the xylenes was lower with a descending trend from p-xylene to o-xylene.

According to the lower volatility of the xylenes (Table 1), with respectively vapor pressure of 5.75, 6.25 and 5.9 mm Hg at 20°C for o-xylene, m-xylene and p-xylene (Kassel, 1936), it is concluded that the degradation main factor should be the free radicals on the surface of the metallic nanoparticles. Thus, the compounds with lower volatility, for instance o-xylene, had more fortune to reaction with the free radicals regarding to its more adsorption to the bed's surface and in the beds with more catalytic activity (i.e., ZVI-CZ and C-CZ), it has the most elimination performance. It is showed in other research that xylenes were more adsorbed on the catalyst surface than benzene and toluene (Larson and Falconer, 1997).

It is found that the $^{\bullet}OH$ predominantly adds to the unsubstituted ring positions of xylenes (Fig. 5), similar to toluene's reaction and abstraction of H from the methyl groups and addition at the substituted positions are not so important. Because of high reactivity of the $^{\bullet}OH$ radical, it is added to the electron-rich sites in the aromatic ring producing the dimethyl-hydroxyl-cyclo hexa-dienyl radicals which are oxidized by ferricyanide and forming dimethylphenols (Albarran and Munguia, 2014).

Loading rate of the BTXs: With the results for BTXs inlet and outlet concentrations and applying a mass balance for them, the loaded and removed pollution mass per unit volume of the bed was found as $\mu g\ cm^{-3}$ of be per hour ($\mu g\ cm^{-3}$ B.h) (Fig. 6). Bars in the figure represent the remained pollution loading as not degraded in the exhaust air of each bed. For example about benzene, up to 54.5 $\mu g\ cm^{-3}$ B.h was obtained by ZVI-CZ compared to C-CZ and CO-CZ, respectively with 29.3 and 12.7 $\mu g\ cm^{-3}$ B.h. According to the other studies such as photocatalytic removal of BTEXs (Martinez *et al*., 2014), these are much higher loading and removal rates which show more capability of this system for higher concentration conditions.

Mineralization of the BTXs: The Inlet concentration of CO_2 was constantly equal to 500 ppm and the outlet concentration for ZVI-CZ, CO-CZ and C-CZ respectively were 650, 550 and 750 ppm. The mineralization (i.e., conversion of the pollutants to CO_2 and H_2O) was resulted from the obtained CO_2 and BTXs loading mass balance. These results indicated that the Mineralization/Elimination (M/E) ratio of BTXs was up to 0.83 on C-CZ, so, it was more than ZVI-CZ and CO-CZ with 0.58 and 0.37 (Fig. 7). The up/down bars in the figure show the amount of remained pollutants as intermediate compounds.

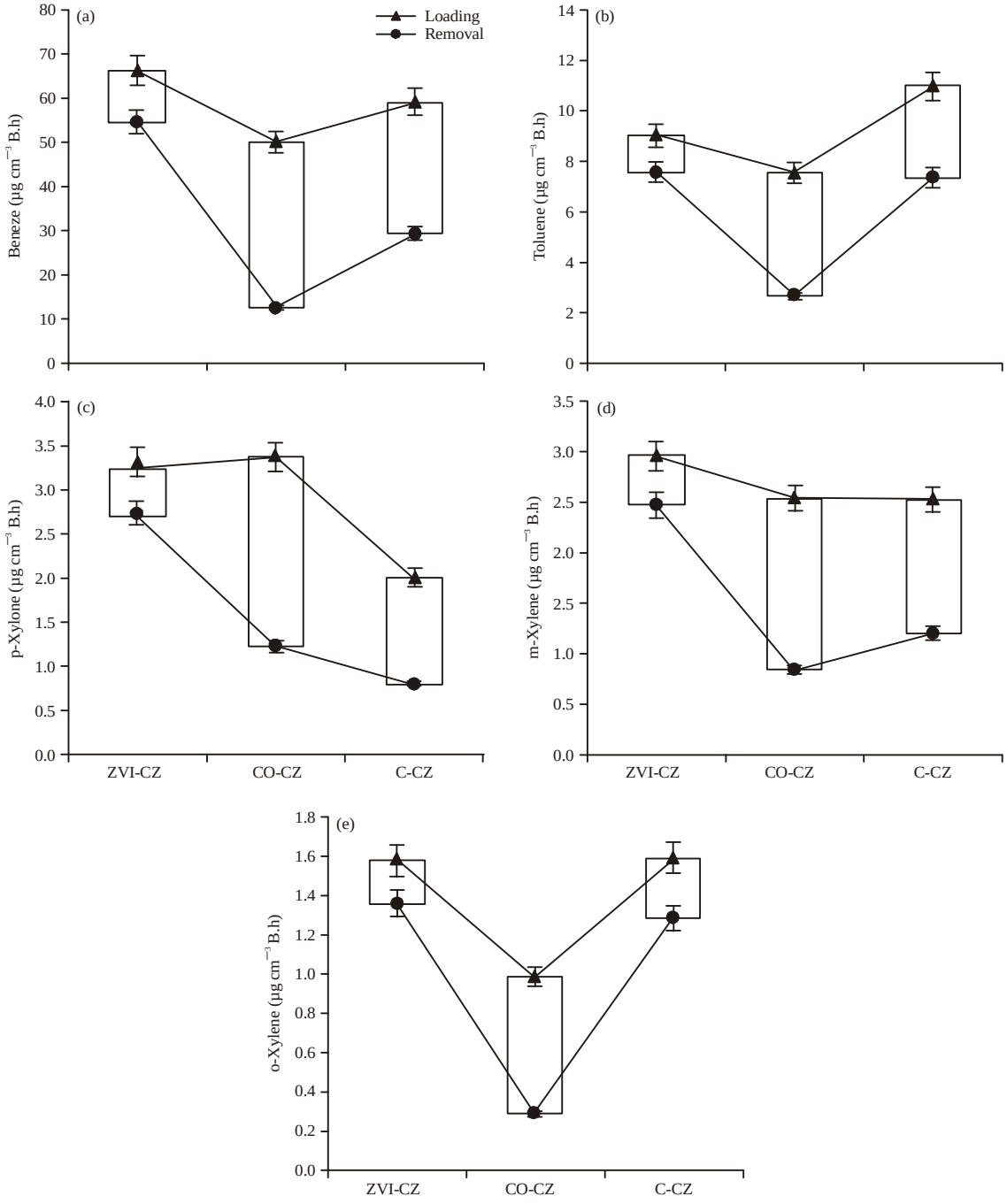

Fig. 6(a-e): Loading and removal mass of pollutants on the coated beds, (a) Benzene, (b) Toulene, (c) p-Xylene, (d) m-Xylene and (e) o-Xylene

With the results, C-CZ showed the most mineralization/elimination ratio. So, we can say that the Fe^0 nanoparticles could destruct more mass of VOCs and a combination of Fe^0 and Cu_2O nanoparticles eliminates less mass of VOCs; but, the combined one (i.e., C-CZ) destruct a greater portion of the eliminated VOCs to CO_2. This could be related to the presence of Fe^0 and Cu_2O with

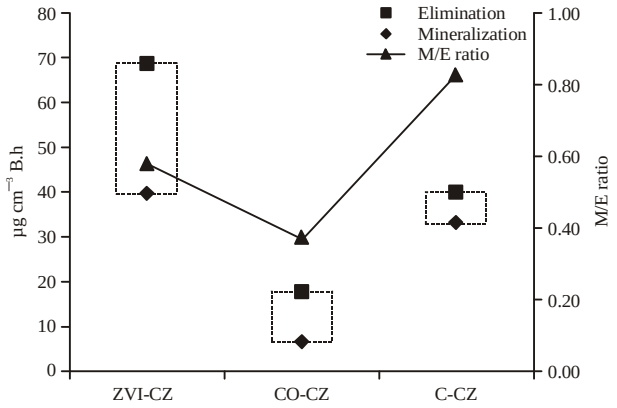

Fig. 7: BTXs elimination and mineralization on the coated zeolites

the different oxidation and reduction properties, more production of free radicals and affinity of the pollutants to adsorption on the catalyst bed (Wang *et al*., 2008). Thereupon, the Cu_2O can act as a good electron transmitter that could increase free radical formation (Pham and Lee, 2014) which could react with the intermediates to more completely degradation; although, Cu_2O was itself a weaker catalyst for BTXs degradation and has led to lower decomposition rate in C-CZ. The obtained mineralization rate is considerable according to the experiment conditions; so that, Everaert and Baeyens (2004) reported a full conversion of VOCs by thermo-catalytic process at 260-340°C with feed concentrations of 30-60 ppm (Everaert and Baeyens, 2004). The concentration in the present study was more than 60 ppm (Table 2) and the temperature was lower than 260°C; however, full conversion of a notable fraction of VOCs is obtained specially by C-CZ.

CONCLUSION

The result of this study showed that the Fe^0 nanoparticles are more effective than Cu_2O to destruct the VOCs and significantly enhanced the catalytic properties of the natural zeolite which was used in this study (i.e., Clinoptilolite). A combination of Fe^0 and Cu_2O nanoparticles may offer simultaneously higher free radicals formation which will result in more degradation of intermediate compounds. So, it has a synergetic effect on VOCs mineralization and its M/E ratio is higher than Fe^0, but can eliminate less mass of the VOCs. As the catalyst nanoparticles are on zeolite surface and catalytic destruction of the pollutants are mainly take place at the surface, the VOCs with higher volatility such as benzene were lower eliminated in this process.

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REFERENCES

Albarran, G. and J.S. Munguia, 2014. Radiolytic Oxidation of Xylenes by radical and dot; OH Radicals Radiat. Phys. Chem., 97: 90-94.

Asilian, H., S.B. Mortazavi, H. Kazemian, S. Phaghihzadeh, S. Shahtaheri and M. Salem, 2004. Removal of ammonia from air, using three Iranian natural zeolite. Iran. J. Publ. Health, 33: 45-51.

Benzinger, S.B., 2010. Reaction of hydroxyl radical with aromatic hydrocarbons. Master's Thesis, Ball State University.

Berndt, T., O. Boge and H. Herrmann, 1999. On the formation of benzene oxide/oxepin in the gas-phase reaction of OH radicals with benzene. Chem. Phys. Lett., 314: 435-442.

Braja, M.D., 2001. Soil Mechanics Laboratory Manual. Oxford University Press, Oxford, UK.

Davil, M.F., R. Rostami, A. Zarei, M. Feizizadeh and M. Mahdavi *et al*., 2011. A survey of 24 hour variations of BTEX concentration in the ambient air of Tehran. J. Babol Univ. Med. Sci., 14: 50-55.

Everaert, K. and J. Baeyens, 2004. Catalytic combustion of volatile organic compounds. J. Hazard. Mater., 109: 113-139.

Giroir-Fendler, A., S. Gil, J.A. Diaz, L. Retailleau-Mevel, M. Ousmane, T.M. Pera and C.F. De, 2014. Catalytic combustion of toluene over cryptomelane-type manganese oxide supported metals. Proceedings of the 8th International Conference on Environmental Catalysis, September 16-20, 2014, Italy.

Golding, B.T., M.L. Barnes, C. Bleasdale, A.P. Henderson and D. Jiang *et al*., 2010. Modeling the formation and reactions of benzene metabolites. Chemico-Biol. Int., 184: 196-200.

Grain, F., 2004. Environmental catalysis. Catal. Today, 89: 255-268.

Grcic, I., S. Papic, K. Zizek and N. Koprivanac, 2012. Zero-Valent Iron (ZVI) Fenton oxidation of reactive dye wastewater under UV-C and solar irradiation. Chem. Eng. J., 195: 77-90.

Guillemot, M., J. Mijoin, S. Mignard and P. Magnoux, 2007. Volatile Organic Compounds (VOCs) removal over dual functional adsorbent/catalyst system. Applied Catal. B: Environ., 75: 249-255.

Hanna, P.M. and R.P. Mason, 1992. Direct evidence for inhibition of free radical formation from Cu(I) and hydrogen peroxide by glutathione and other potential ligands using the EPR spin-trapping technique. Arch. Biochem. Biophys., 295: 205-213.

Henn, K.W. and D.W. Waddill, 2006. Utilization of nanoscale zero-valent iron for source remediation-A case study. Remed. J., 16: 57-77.

Hernandez, M.A., L. Corona, A.I. Gonzalez, F. Rojas, V.H. Lara and F. Silva, 2005. Quantitative study of the adsorption of aromatic hydrocarbons (Benzene, Toluene and p-Xylene) on dealuminated clinoptilolites. Ind. Eng. Chem. Res., 44: 2908-2916.

Hu, S.X., J.G. Yu, S.M. Li and E.Y. Zeng, 2011. Theoretical considerations of secondary organic aerosol formation from H-abstraction of p-xylene. Comput. Theoret. Chem., 977: 13-21.

Huang, M., Z. Wang, L. Hao and W. Zhang, 2011. Theoretical investigation on the mechanism and kinetics of OH radical with m-xylene. Comput. Theoret. Chem., 965: 285-290.

Kassel, L.S., 1936. Vapor pressures of the xylenes and mesitylene1. J. Am. Chem. Soc., 58: 670-671.

Keshavarzi, H., F.S. Halak and M. Mirmohamadi, 2003. Survey and measurement of VOCs in closed domestic ambient and public places. Environ. Stud., 29: 41-46.

Khan, F.I. and A.K. Ghoshal, 2000. Removal of volatile organic compounds from polluted air. J. Loss Prev. Process Ind., 13: 527-545.

Kim, Y.H., W.S. Shin, S.O. Ko and M.C. Kim, 2004. Reduction of aromatic hydrocarbons by zero-valent iron and palladium catalyst. Proceedings of the 227th ACS National Meeting of the American Chemistry Society, Division of Environmental Chemistry, March 28-April 1, 2004, Anaheim, CA., pp: 589-593.

Lai, B., Y.H. Zhang, R. Li, Y.X. Zhou and J. Wang, 2014. Influence of operating temperature on the reduction of high concentration *p*-nitrophenol (PNP) by Zero Valent Iron (ZVI). Chem. Eng. J., 249: 143-152.

Larson, S.A. and J.L. Falconer, 1997. Initial reaction steps in photocatalytic oxidation of aromatics. Catal. Lett., 44: 57-65.

Li, X.Q., D.W. Elliott and W.X. Zhang, 2006. Zero-Valent iron nanoparticles for abatement of environmental pollutants: Materials and engineering aspects. Crit. Rev. Solid State Mater. Sci., 31: 111-122.

Lu, C.Y. and M.Y. Wey, 2007. Simultaneous removal of VOC and NO by activated carbon impregnated with transition metal catalysts in combustion flue gas. Fuel Proces. Technol., 88: 557-567.

Majumdar, D., A.K. Mukherjeea and S. Sen, 2011. BTEX in ambient air of a Metropolitan city. J. Environ. Prot., 2: 11-20.

Martinez, T., A. Bertron, G. Escadeillas, E. Ringot and V. Simon, 2014. BTEX abatement by photocatalytic TiO_2-bearing coatings applied to cement mortars. Build. Environ., 71: 186-192.

McDowall, L., 2005. Degradation of toxic chemicals by zero-valent metal nanoparticles: A literature review. Department of Defence, Australian Government. http://www.ironmountainmine.com/iron%20mountain/zero-valent%20metal%20nanoparticle%20decontaminants.pdf

NIOSH., 2003. NIOSH Manual of Analytical Methods. NIOSH., Atlanta, pp: 2-7.

Nichipor, H., E. Dashouk, S. Yacko, Y. Sun, A.G. Chmielewski, Z. Zimek and S. Bulka, 2012. Kinetic modeling of benzene and toluene decomposition in air and in flue gas under electron beam irradiation. Radiat. Phys. Chem., 81: 572-579.

O'Carroll, D., B. Sleep, M. Krol, H. Boparai and C. Kocur, 2013. Nanoscale zero valent iron and bimetallic particles for contaminated site remediation. Adv. Water Resour., 51: 104-122.

Ohura, T., T. Amagai, X. Shen, S. Li, P. Zhang and L. Zhu, 2009. Comparative study on indoor air quality in Japan and China: Characteristics of residential indoor and outdoor VOCs. Atmos. Environ., 43: 6352-6359.

Papaefthimiou, P., T. Ioannides and X.E. Verykios, 1997. Combustion of non-halogenated volatile organic compounds over group VIII metal catalysts. Applied Catal. B: Environ., 13: 175-184.

Pham, T.D. and B.K. Lee, 2014. Cu doped TiO_2/GF for photocatalytic disinfection of *Escherichia coli* in bioaerosols under visible light irradiation: Application and mechanism. Applied Surface Sci., 296: 15-23.

Piumetti, M., N. Russo and D. Fino, 2014. Complete oxidation of volatile organic compounds over manganese oxide catalysts. Proceedings of the Joint Meeting of the French and Italian Sections-IFRF and The Combustion Institute, April 23-24, 2014, Pisa, Italy.

Qian, Y., X. Zhou, Y. Zhang, W. Zhang and J. Chen, 2013. Performance and properties of nanoscale calcium peroxide for toluene removal. Chemosphere, 91: 717-723.

Rostami, R., A.J. Jafari, R.R. Kalantari and M. Gholami, 2014. Influence of pollution loading and flow rate on catalytic BTEX removal with a combined Cu2O, Fe0/Zeolite bed. Iran. J. Health Saf. Environ., 1: 9-15.

Scire, S., S. Minico, C. Crisafulli, C. Satriano and A. Pistone, 2003. Catalytic combustion of volatile organic compounds on gold/cerium oxide catalysts. Applied Catalysis B: Environ., 40: 43-49.

Semadeni, M., 1994. Hydroxyl radical reactions with volatile organic compounds under simulated tropospheric conditions: Tropospheric lifetimes. Ph.D. Thesis, ETH Institutional, Zurich.

Shen, J.H., Y.S. Wang, J.P. Lin, S.H. Wu and J.J. Horng, 2014. Improving the indoor air quality of respiratory type of medical facility by zeolite filtering. J. Air Waste Manage. Assoc., 64: 13-18.

Silva, E., R. Catalao, J. Silva, F. Vaz and F. Oliveira *et al*., 2008. Zeolite-Coated Ceramic Foams for VOCs Removal. In: Studies in Surface Science and Catalysis, Gedeon, P.M.A. and B. Florence (Eds.). Vol. 174, Elsevier, UK., pp: 1195-1198.

Sim, J.K., H.O. Seo, M.G. Jeong, K.D. Kim, Y.D. Kim and D.C. Lim, 2013. Catalytic NiO filter supported on carbon fiber for oxidation of volatile organic compounds. Bull. Korean Chem. Soc., 34: 2105-2110.

Tratnyek, P.G., T.L. Johnson, M.M. Scherer and G.R. Eykholt, 1997. Remediating ground water with zero-valent metals: Chemical considerations in barrier design. Groundwater Monitor. Remediation, 17: 108-114.

Van Durme, J., J. Dewulf, W. Sysmans, C. Leys and H. Van Langenhove, 2007. Abatement and degradation pathways of toluene in indoor air by positive corona discharge. Chemosphere, 68: 1821-1829.

Vivanco, M.G. and M. Santiago, 2010. Secondary Organic Aerosol Formation from the Oxidation of a Mixture of Organic Gases in a Chamber. In: Air Quality, Kuma, A. (Ed.). Sciyo, Spain.

Volkamer, R., B. Klotz, I. Barnes, T. Imamura and K. Wirtz *et al*., 2002. OH-initiated oxidation of benzene Part I. Phenol formation under atmospheric conditions. Phys. Chem. Chem. Phys., 4: 1598-1610.

Wang, A., X. Li, Y. Zhao, W. Wu, J. Chen and H. Meng, 2014. Preparation and characterizations of Cu_2O/reduced graphene oxide nanocomposites with high photo-catalytic performances. Powder Technol., 261: 42-48.

Wang, B., J.J. Yin, X. Zhou, I. Kurash, Z. Chai, Y. Zhao and W. Feng, 2012. Physicochemical origin for free radical generation of iron oxide nanoparticles in biomicroenvironment: Catalytic activities mediated by surface chemical states. J. Phys. Chem. C, 117: 383-392.

Wang, J., C.H. Li and T.J. Huang, 2005. Study of partial oxidative steam reforming of methanol over Cu-ZnO/samaria-doped ceria catalyst. Catalysis Lett., 103: 239-247.

Wang, S.P., T.Y. Zhang, Y. Su, S.R. Wang, S.M. Zhang, B.L. Zhu and S.H. Wu, 2008. An investigation of catalytic activity for CO oxidation of $CuO/Ce_x\ Zr_{1-x}\ O_2$ catalysts. Catal. Lett., 121: 70-76.

Zhang, W.X., 2003. Nanoscale iron particles for environmental remediation: An overview. J. Nanoparticle Res., 5: 323-332.

Zhao, J., R. Zhang, K. Misawa and K. Shibuya, 2005. Experimental product study of the OH-initiated oxidation of m-xylene. J. Photochem. Photobiol. A: Chem., 176: 199-207.

Ziemann, P.J. and R. Atkinson, 2012. Kinetics, products and mechanisms of secondary organic aerosol formation. Chem. Soc. Rev., 41: 6582-6605.